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# EFFECT OF HEATING RATE ON THE PHYSICOMECHANICAL PROPERTIES OF SILICEOUS CERAMICS

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The effect of heating rate on the density, water absorption, and the Young's modulus of ceramic materials based on clays of different mineralogic compositions is studied. It is established that the optimum heating rate depends on the mineralogic composition and the functional parameters of ceramics.

Firing is the most power-consuming technological operation in ceramic production. Imperfect firing conditions result in a significant excess in energy consumption. According to the data in [1], the power consumption per 1 kg of ceramic products in the CIS countries is on the average 1.6 times higher than the same parameter abroad. The main reason for this excessive consumption is the insufficient knowledge of the heat and mass transfer process complicated by phase and chemical transformations in the fired articles, and the absence of reliable data on the thermophysical properties of materials and their modification in firing.

The existing mathematical models of heat treatment of ceramic articles and methods for designing firing conditions do not always enable one to take into account the effect of the specified factors on heat transfer processes and distinguish the main factors, i.e., to design the firing conditions [1]. Therefore, there is currently no sufficiently precise method for calculating firing conditions of ceramic products, especially when the material is based on polymineral argillaceous mixtures. There are several experimental methods and formulas which can be used to calculate the duration of the heat treatment process for certain temperature intervals, but they are insufficiently precise to develop firing regimes for workpieces made of specific mixtures.

It was observed that the heating rate is the determining factor, since the products are traditionally cooled together with the furnace. The heating rate has a significant effect on the physicomechanical processes occurring in the firing of clays and ceramic mixtures. An increase in the heating rate decreases the clay viscosity, which increases the number of melts of different compositions and structures [2]. However, the heating rate has to be limited in order to avoid an excessive temperature difference between the surface and the inner layers of the article. Otherwise, the melt will fill the pores in

the outer layer before the organic compound burns out in the depth of the mixture. Phase transformations and exothermic and endothermic chemical reactions have a great effect on the actual temperature in different parts of the sample. As the heating rate increases, the thermal effects are shifted to the higher temperature region and thus significantly modify the sintering mechanism of ceramic articles [2].

In this context, we carried out systematic experimental studies whose purpose was to investigate the effect of the heating rate on the physicomechanical properties of sintered ceramic mixtures made of different clays. The experimentally found parameters made it possible to calculate the optimum firing conditions, or at least to narrow the search interval for specific material compositions. It is known that different properties of the same material attain their optimum values under different heat-treating conditions. Therefore, the "optimum" properties are generally understood as specific functional characteristics. In our case, the selected parameters were water absorption, density, the elasticity modulus, and thermal resistance.

The ceramic mixture M1 selected for investigation consisted of two components: pegmatite (35 – 37%) and clay from the Kara-Keche deposit (63 – 65%). The mineralogical composition of the mixture (wt.%) was 28 – 30 quartz, 59 – 60 kaolin, and 8 – 10 hydromica. The chemical composition was (%) 72.86 $SiO_2$, 22.86 $Al_2O_3$, 1.11 $Fe_2O_3$, 1.22 $TiO_2$, 0.48 CaO, and 1.53 MgO, $K_2O$, $Na_2O$. The mixture M2 used for reference purposes was based on the refractory clay from the Arkalyk deposit and contained (%) 56.13 $SiO_2$, 38.42 $Al_2O_3$, 1.48 $Fe_2O_3$, 1.62 $TiO_2$, 0.48 CaO, and 1.87 MgO, $K_2O$, $Na_2O$.

Cylinder-shaped samples 10 mm in diameter and 110 mm long produced by screw molding were dried to a constant weight at a temperature of 380 – 390 K, then fired in a SNOL-type muffle furnace at a temperature of 1373 K for 1 h.

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Three separate heating regimes were consecutively used: a uniform increase in temperature at rates 0.05, 0.20, and 0.40 K/sec, respectively.

The fired samples were analyzed for shrinkage, water absorption, apparent density, and mechanical strength,

Mechanical strength was determined from the Young's modulus $E$ in accordance with GOST 24409–80. The values of $E$ were determined by the three-point bending method from the formula

$$E = \frac{l^3 \Delta F}{48 J \Delta y},$$

where $l$ is the distance between the prisms; $F$ is the bending force; $J = \pi d^4/64$ is the axial moment of inertia of the sample lateral section with the diameter $d$; $y$ is the sample deflection.

The thermal resistance was determined by the temperature which in combination with subsequent rapid cooling decreased the strength of the material to one-third (GOST 24409–80).

Analysis of the measurement results shown in Table 1 reveals that the heating rates affect unequally the properties of ceramic materials made of different clays.

An increase in the heating rate from 0.05 to 0.40 K for mixture M1 decreases the water absorption and increases the apparent density and the strength. In this case, the Young's modulus and the water absorption vary linearly with increasing heating rate, and the density grows fastest within the heating rate interval 0.20 to 0.40 K/sec.

The strength of ceramics based on M2 mixture decreases with increasing heating rate, which is especially evident while the latter increases from 0.20 to 0.40 K/sec. The water absorption virtually does not depend on the heating rate, and the open porosity remains high (15%). No relationship was found between the weight loss and shrinkage and the heating rate. M1 mixture exhibits higher weight loss.

M1 and M2 mixtures can be classified as different types with respect to the effect of the heating rate on their firing properties. The first type includes M1 mixture whose strength and density improves with increasing heating rate,

and the second type includes M2 mixture whose properties either deteriorate or remain unchanged. This distinction agrees with the mineralogic compositions of the clays: the main components of M1 mixture are kaolinite and hydromica, and the main component of M2 mixture is montmorillonite. According to the data in [3], as heating rate of kaolinite-hydromica clays increases, the water absorption of the latter decreases, and their shrinkage, apparent strength, and density increase. The shrinkage and strength of the montmorillonite clays decrease, whereas their water absorption grows.

The absence of correlation of some parameters to the heating rate is accounted by the heterogeneous sample structure across the section. The structure formation in firing is determined by the initial mixture parameters, as well as by the velocity of the thermal front migration inside the sample. The samples of M1 mixture fired at a heating rate of 0.05 K/sec have a homogeneously colored and structured fracture. The sections of the M1 samples fired at 0.20 and 0.40 K/sec represent the densely sintered ceramic circles (sintered according to the liquid/solid phase mechanism, i.e., liquid phase – glass), inside which the black areas with large pores can be seen. The main cause for the emergence of the black sites is the iron oxide reduction: $Fe_2O_3 \rightarrow FeO$ [3]; FeO is a strong flux; therefore, a greater amount of the vitreous phase is formed inside the article, whereas $SiO_2$ and $Al_2O_3$, which decrease the thermal expansion of material, are dissolved in that phase.

Judging from the Young's modulus values given in Table 1, the described processes facilitate attaining the maximum strength in the M1 mixture samples under fast heating. The samples fired at a heating rate of 0.20 K/sec have a similar structure; however, their sintered outer layer is thinner (70 and 50%, respectively).

The high values of the lattice energy and the melting point of the M2 mixture, which contains 35 $Al_2O_3$, contribute to increased strength of the sample; the sintering is implemented according to the solid-phase mechanism, and an increase in the heating rate impedes the consolidation of particles and the development of polymorphous transformations.

The depth of penetration of the thermal front in the M2 samples depends on the temperature, the firing duration, and the heating rate. It can be determined by the color of the sites (beige-pink or gray) in the sample lateral section. Each site has a structure determined by the maximum local temperature. Thus, a clearly perceptible pink area points to the presence of phase transformations. The depth of the heat front penetration (%) was assessed by the formula

$$\Delta = (r/R) \times 100,$$

where $r$ is the distance between the sample surface and the boundary between the pink and the gray areas; $R$ is the sample radius.

**TABLE 1**

| Parameter | Ceramics made of mixture: | | | | | |
|---|---|---|---|---|---|---|
| | M1 at heating rate, K/sec | | | M2 at heating rate, K/sec | | |
| | 0.05 | 0.20 | 0.40 | 0.05 | 0.20 | 0.40 |
| Mass loss, % | 9.0 | 8.0 | 11.0 | 7.8 | 8.0 | 7.8 |
| Water absorption, % | 16.0 | 7.5 | 3.4 | 17.2 | 13.0 | 15.5 |
| Shrinkage, % | 8.5 | 2.0 | 5.0 | 2.7 | 5.0 | 3.0 |
| Apparent density, kg/m$^3$ | 2000 | 2030 | 2240 | 1930 | 2010 | 1820 |
| Young's modulus, GPa | 20 | 40 | 60 | 50 | 45 | 26 |

Table 2 presents the values $\Delta$ of penetration of the thermal front across the sample section at the heating rate of 0.40 K/sec. Three lots of M2 samples were studied within the temperature range of 873 – 1373 K with holding of 0.1 and 2 h.

As can be seen, an increase in temperature by 100 K results in the advance of the thermal front by less than 10%, and an increase in the holding duration from 0 to 2 h increases the front penetration by more than 15%.

It is established that the most homogeneously colored structure is formed at a heating rate of 0.05 K/sec. However, the firing regime at the temperature of 1373 K and 1 h holding is insufficient for high-quality sintering of M2 mixture, which is testified to by the low values of the Young's modulus. The Young's modulus of M1 mixture increases in proportion to the heating rate, and for M2 mixture, the lowest possible heating rate is desirable.

The effect of the firing temperature on the Young's modulus of M1 and M2 samples fired at the optimum heating rates (0.40 and 0.05 K/sec, respectively) was investigated (Table 3).

The Young's modulus of the sample made of M2 mixture reaches 95 GPa at the firing temperature of 1523 K, which is an indication of the refractory properties of the mixture. Due to the low melting point of the Kara-Keche clay (1513 K) whose sintering occurs at 1373 K, the Young's modulus of the M1 mixture sample does not exceed 50 GPa.

The Young's modulus expresses the elastic deformation resistance, which is a measure of the strength and the force of the interatomic bond [4]. This parameter in ceramics to a great extent depends on the porosity. In the general case

$$E = E_0(1 - a\Pi),$$

where $E$ is the Young's modulus of the poreless material; $a$ is the coefficient; $\Pi$ is the porosity.

The values of $E$ in the M1 samples are directly proportional to density and inversely proportional to porosity for any heating rate. The theoretical value of the Young's modulus for poreless ceramics $E_0 = 70$ GPa, $a = 4$. Apparently, by modifying the heating rate in the vicinity of 0.05 K/sec, it is possible to obtain a sample with a homogeneous structure and the maximum strength while maintaining the same firing regime.

The optimum heating rate for M2 mixture samples is 0.05 K/sec, whereas $E_0 = 175$ GPa, $a = 4.2$. The increase in the Young's modulus with increasing temperature is determined by the consolidation of particles and the evolution of polymorphous transformations. As the heating rate increases from 0.20 to 0.40 K/sec, the values of $a$ grow from 5.7 to 6.4, respectively. This points to the increased structural sensitivity of the mechanical properties of the material.

**TABLE 2**

| Firing temperature, K | Depth of penetration of thermal front, %, at holding, h | | |
|---|---|---|---|
| | 0 | 1 | 2 |
| 873 | 35 | 42 | 56 |
| 973 | 42 | 58 | 60 |
| 1073 | 58 | 70 | 72 |
| 1173 | 60 | 63 | 75 |
| 1273 | 65 | 80 | 90 |
| 1373 | 70 | 85 | 95 |

**TABLE 3**

| Sample of mixture | Young's modulus, GPa, at firing temperature, K | | | |
|---|---|---|---|---|
| | 1173 | 1273 | 1373 | 1523 |
| M1 | 15 | 15 | 50 | – |
| M2 | 10 | 20 | 45 | 95 |

The thermal resistance of M1 mixture samples exceeds $\Delta T = 500$ K for both values of the heating rate. The low Young's modulus values of M2 samples indirectly confirm the formation of a poorly sintered cracked structure, which regularly does not exhibit jumpwise growth of cracks and a decrease strength with increasing $\Delta T$. The strength of the samples of M2 mixture at $\Delta T = 300$ K decreases by 20%. The optimization of the firing regimes for these samples can significantly increase their strength and decrease the heat resistance, or vice versa.

The optimum firing conditions (temperature, heating duration, and heating rate) have to be selected in compliance with the main functional parameters of ceramics. Optimization of the firing regimes and prediction of the properties of ceramic materials will be possible only when experiments are conducted to give substitution coefficients for semi-empirical formulas and subsequent designs.

**REFERENCES**

1. S. A. Karaush, E. G. Bober', and Yu. I. Chizhik, "Calculation of temperature fields in fired ceramic articles," *Steklo Keram.*, No. 6, 13 – 15 (1996).
2. Yu. Tikhi, *Firing of Ceramics* [Russian translation], Stroiizdat, Moscow (1988).
3. V. F. Pavlov, *Physicochemical Principles of Firing Articles of Construction Ceramics* [in Russian], Stroiizdat, Moscow (1976).
4. G. N. Maslennikova, R. A. Mamaladze, S. Midzuta, and K. Koumoto, *Ceramic Materials* [in Russian], Stroiizdat, Moscow (1991).